

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
2 May 2002 (02.05.2002)

PCT

(10) International Publication Number
WO 02/34870 A1

(51) International Patent Classification⁷: C11D 3/37, 3/36

(21) International Application Number: PCT/EP01/12083

(22) International Filing Date: 17 October 2001 (17.10.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
00309395.2 25 October 2000 (25.10.2000) EP

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(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: DISH-WASHING COMPOSITIONS

(57) Abstract: A machine dish wash composition comprising: a) a hydrophobically modified polycarboxylic acid b) an organic phosphonates and c) a polymer of acrylic acid.

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DISH-WASHING COMPOSITIONS

The present invention is in the field of machine dishwashing. More specifically, the invention encompasses compositions for use in a machine dish wash formulation, which do not necessitate the addition of salt or rinse aid to the machine.

To wash articles in a commercially available dish washing machine entails using three product types. Salt is added to the salt compartment to soften the water, a dishwashing formulation is used to clean the articles and a rinse aid is used to ensure that the articles are rinsed with no streaks or smears.

Consumers find it inconvenient replace the salt and rinse aid in a dish wash machine.

WO 00/06684 (Benckiser) discloses a machine dish wash tablet. The tablet has a base composition that carries out its function in the main wash cycle, and a separate core that acts as a rinse aid in the rinse cycle of the machine. However such a tablet is complicated to manufacture.

The present invention relates to a composition for washing dishes that obviates the need for salt and rinse aid in the machine dishwashing process.

Accordingly, the present invention relates to a machine dish wash composition comprising:

- a) a hydrophobically modified polycarboxylic acid
- b) an organic phosphonates and
- c) a polymer of acrylic acid.

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Also described is a process for washing articles in a dishwasher comprising the steps of:

- i) adding a composition as described in the preceding paragraph to the wash liquor of the dishwasher followed by;
- ii) treating articles requiring cleaning with the wash liquor in a conventional manner;

wherein no additional rinse aid is present within the dishwasher and no salt is present in the dishwasher to rejuvenate the ion exchange.

Also part of this inventive concept is a kit of parts comprising a composition as described above and instructions stating that no rinse aid or salt is to be added to the dishwashing machine.

Compositions according to the invention have been found to be particularly effective at antiscaling and antispotting in the machine dishwash process. In particular, with the inclusion of relatively high levels of hydrophobically modified polycarboxylic acid, this can lead to a cloudy surface appearing on e.g. glass. However the combination of ingredients which is the invention addressed these problems. A combination of antiscaling/antispotting agents are present in the composition of the invention.

The first is a hydrophobically modified polycarboxylic acid, preferably a co-polymer containing as polymerised units from 20 to 75 wt% maleic acid, maleic anhydride or salts thereof and from 25 to 80 wt% of a hydrophobe which is at least one monomer selected from the group consisting of isobutylene, diisobutylene, styrene, decane and eicosene.

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The hydrophobically modified polycarboxylic acid preferably has a molecular weight from 200 to 1 million, more preferably from 1,000 to 750,000.

- 5 A preferred hydrophobically modified polycarboxylic acid is Acusol 820, a copolymer of acrylic acid with C₁₈ and with EO₂₀C₁₈ side chains, MW about 500,000, supplied by Rohm and Haas Company; particularly preferred is Acusol 460, a co-polymer of diisobutylene and maleic acid, MW 15,000,
10 supplied by Rohm and Haas Company;

- It is preferable if the level of hydrophobically modified polycarboxylic acid is from 0.1 to 10 wt% of the total composition, more preferably from 0.5 to 7 wt%, most
15 preferably from 1 to 5 wt%. However in certain preferred embodiments, the preferred range of modified polycarboxylic acid may be from 0.1% to 10%, preferably 0.15 to 1.0%, even more preferably 0.3 to 0.6% by weight of the composition.

- 20 Organic phosphonates are also present as antiscaling agents.

- Particularly preferred antiscaling agents are organic phosphonates such as α -hydroxy-2 phenyl ethyl diphosphonate, ethylene diphosphonate, hydroxy 1,1-hexylidene, vinylidene
25 1,1 diphosphonate, 1,2 dihydroxyethane 1,1 diphosphonate and hydroxy-ethylene 1,1 diphosphonate. Most preferred is hydroxy-ethylene 1,1 diphosphonate (EDHP) and 2 phosphonobutane, 1,2,4 tricarboxylic acid (Bayhibit).

- 30 Also present are polymers and co-polymers of acrylic acid having a molecular weight between 500 and 20,000 can also be used, such as homo-polymeric polycarboxylic acid compounds with acrylic acid as the monomeric unit. The average weight of such homo-polymers in the acid form preferably ranges
35 from 1,000 to 100,000 particularly from 3,000 to 10,000.

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Also suitable are polymeric polycarboxylates are co-polymers derived from monomers of acrylic acid and maleic acid. The average molecular weight of these polymers in the acid form preferably ranges from 4,000 to 70,000.

It is preferable if the level antiscaling agent is from 0.2 to 10 wt% of the total composition, preferably from 0.5 to 5 wt%.

Preferred ratios of antiscaling agent to nonionic surfactant are 1:3 to 3:1, more preferably 1:1 to 1:2

Surfactant System

The composition also comprises a surfactant system, which preferably comprises ethoxylated and/or propoxylated nonionic surfactants, more preferably selected from nonionic ethoxylated/propoxylated fatty alcohol surfactants which preferably have a cloud point in water of 14 or less, preferably of 12 or less, most preferably 10°C or less.

Examples of suitable nonionic surfactants having the required cloud points for use in the invention are found in the low- to non-foaming ethoxylated straight-chain alcohols of the Plurafac® LF series, supplied by the BASF Company; Synperonic RA series supplied by ICI Triton® DF series, supplied by the Rohm & Haas Company.

Other suitable surfactants include epoxy capped poly (oxyalkylated) alcohols, such as e.g. SLB 18B 45, ex. Olin Chemicals.

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The surfactants are preferably present at levels of at least 4.0 wt%, preferably 4-6 wt%, more preferably 5 to 8 wt% of the total composition.

- 5 An antifoam to suppress foaming is preferably present.

If an anionic surfactant is used it is advantageously present at levels of 2 wt% or below.

10 Builder Material

The compositions of the invention may contain a builder. The builder may be a phosphate or non-phosphate builder.

- 15 Compositions of the invention preferably comprise a water-soluble phosphate builder.

Phosphate builders are particularly preferred. Specific examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerisation ranges from about 6 to 21, and salts of phytic acid. Sodium or potassium tripolyphosphate is most preferred.

- 25 The level of builder is from 35% to 90%, preferably 50% to 90% by weight, preferably from 55% to 80% by weight.

The compositions of the present invention may comprise a water-soluble non-phosphate builder. Suitable examples of non-phosphorus-containing inorganic builders include water-soluble alkali metal carbonates, bicarbonates, sesquicarbonates, borates, silicates, including layered silicates such as SKS-6 ex. Clarent and metasilicates.

35 Specific examples include sodium carbonate (with or without

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calcite seeds), potassium carbonate, sodium and potassium bicarbonates and silicates including layered silicates.

Organic detergent builders can also be used as nonphosphate builders in the present invention. Examples of organic builders include alkali metal citrates, succinates, malonates, fatty acid sulfonates, fatty acid carboxylates, nitrilotriacetates, oxydisuccinates, alkyl and alkenyl disuccinates, oxydiacetates, carboxymethyloxy succinates, ethylenediamine tetraacetates, tartrate monosuccinates, tartrate disuccinates, tartrate monoacetates, tartrate diacetates, oxidised starches, oxidised heteropolymeric polysaccharides, polyhydroxysulfonates, polycarboxylates such as polyacrylates, polymaleates, polyacetates, polyhydroxyacrylates, polyacrylate/polymaleate and polyacrylate/ polymethacrylate copolymers, acrylate/maleate/vinyl alcohol terpolymers, aminopolycarboxylates and polyacetal carboxylates, and polyaspartates and mixtures thereof. Such carboxylates are described in U.S. Patent Nos. 4,144,226, 4,146,495 and 4,686,062. Alkali metal citrates, nitrilotriacetates, oxydisuccinates, acrylate/maleate copolymers and acrylate/maleate/vinyl alcohol terpolymers are especially preferred nonphosphate builders.

Silica

Silica material may be included in the composition. Suitable forms of silica include amorphous silica, such as precipitated silica, pyrogenic silica and silica gels, such as hydrogels, xerogels and aerogels, or the pure crystal forms quartz, tridymite or cristobalite, but the amorphous forms of silica are preferred. Suitable silicas may readily be obtained commercially. They are sold, for example under the Registered Trade Name Gasil 200 (ex Crosfield, UK).

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Preferably, the silica is in the product in such a form that it can dissolve when added to the wash liquor. Therefore, addition of silica by way of addition anti-foam particles of silica and silicone oil is not preferred.

Therefore, it is preferred that silica material are used that have a particle size (as determined with a Malvern Laser, i.e. "aggregated" particles size) of at most $40\mu\text{m}$, most preferably at most $20\mu\text{m}$ provides better results in the wash. In view of incorporation in a cleaning composition, it is preferred that the particle size of the silica material is at least $1\mu\text{m}$, more preferably at least $2\mu\text{m}$, and most preferably at least $5\mu\text{m}$.

Preferably, the silica material is present in the cleaning composition at a level of at least 0.1%, more preferably at least 0.5%, most preferably at least 1% by weight of the cleaning composition and preferably at most 10%, more preferably at most 8%, most preferably at most 5% by weight of the cleaning composition.

Silicates

The composition optionally comprises alkali metal silicates. When silicates are present, the SiO_2 level should be from 1% to 35%, preferably from 2% to 20%, more preferably from 3% to 10%, based on the weight of the automatic dishwasher detergent. The ratio of SiO_2 to the alkali metal oxide (M_2O , where M = alkali metal) is typically from 1 to 3.5, preferably from 1.6 to 3, more preferably from 2 to 2.8. Preferably, the alkali metal silicate is hydrous, having from 15% to 25% water, more preferably from 17% to 20%.

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The highly alkali metasilicates can in general be employed, although the less alkaline hydrous alkali metal silicates having a $\text{SiO}_2:\text{M}_2\text{O}$ ratio of from 2.0 to 2.4 are, as noted, greatly preferred. Anhydrous forms of the alkali metal
5 silicates with a $\text{SiO}_2:\text{M}_2\text{O}$ ratio of 2.0 or more are also less preferred because they tend to be significantly less soluble than the hydrous alkali metal silicates having the same ratio.

10 Sodium and potassium, and especially sodium, silicates are preferred. A particularly preferred alkali metal silicate is a granular hydrous sodium silicate having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of from 2.0 to 2.4 available from PQ Corporation, named Britesil H20 and Britesil H24. Most preferred is a
15 granular hydrous sodium silicate having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of 2.0. While typical forms, i.e. powder and granular, of hydrous silicate particles are suitable, preferred silicate particles having a mean particle size between 300 and 900 microns and less than 40% smaller than 150 microns and less
20 than 5% larger than 1700 microns. Particularly preferred is a silicate particle with a mean particle size between 400 and 700 microns with less than 20% smaller than 150 microns and less than 1% larger than 1700 microns. Compositions of the present invention having a pH of 9 or less preferably
25 will be substantially free of alkali metal silicate.

Enzymes

Enzymes may be present in the compositions of the invention.
30 Examples of enzymes suitable for use in the cleaning compositions of this invention include lipases, peptidases, amylases (amylolytic enzymes) and others which degrade, alter or facilitate the degradation or alteration of biochemical soils and stains encountered in cleansing
35 situations so as to remove more easily the soil or stain

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from the object being washed to make the soil or stain more removable in a subsequent cleansing step. Both degradation and alteration can improve soil removal.

- 5 Well-known and preferred examples of these enzymes are lipases, amylases and proteases. The enzymes most commonly used in machine dishwashing compositions are amylolytic enzymes. Preferably, the composition of the invention also contains a proteolytic enzyme. Enzymes may be present in a
10 weight percentage amount of from 0.2 to 7% by weight. For amylolytic enzymes, the final composition will have amylolytic activity of from 10^2 to 10^6 Maltose units/kg. For proteolytic enzymes the final composition will have proteolytic enzyme activity of from 10^6 to 10^9 Glycine
15 Units/kg.

Bleach Material

- 20 Bleach material is preferably incorporated in the composition.

The bleach material may be a chlorine- or bromine-releasing agent or a peroxygen compound. Peroxygen-based bleach materials are however preferred.

25

- Organic peroxy acids or the precursors therefor are typically utilized as the bleach material. The peroxyacids usable in the present invention are solid and, preferably, substantially water-insoluble compounds. By "substantially
30 water-insoluble" is meant herein a water-solubility of less than about 1% by weight at ambient temperature. In general, peroxyacids containing at least about 7 carbon atoms are sufficiently insoluble in water for use herein.

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Inorganic peroxygen-generating compounds are also typically used as the bleaching material of the present invention. Examples of these materials are salts of monopersulphate, perborate monohydrate, perborate tetrahydrate, and percarbonate.

Monoperoxy acids useful herein include alkyl peroxy acids and aryl peroxyacids such as peroxybenzoic acid and ring-substituted peroxybenzoic acids (e.g. peroxy- α -naphthoic acid); aliphatic and substituted aliphatic monoperoxy acids (e.g. peroxy lauric acid and peroxy stearic acid); and phthaloyl amido peroxy caproic acid (PAP).

Typical diperoxy acids useful herein include alkyl diperoxy acids and aryldiperoxy acids, such as 1,12-di-peroxy-dodecanedioic acid (DPDA); 1,9-diperoxyazelaic acid, diperoxybrassylic acid, diperoxysebacic acid and diperoxy-isophthalic acid; and 2-decyldiperoxybutane-1,4-dioic acid.

Peroxyacid bleach precursors are well known in the art. As non-limiting examples can be named N,N,N',N'-tetraacetyl ethylene diamine (TAED), sodium nonanoyloxybenzene sulphonate (SNOBS), sodium benzoyloxybenzene sulphonate (SBOBS) and the cationic peroxyacid precursor (SPCC) as described in US-A-4,751,015.

If desirably a bleach catalyst, such as the manganese complex, e.g. Mn-Me TACN, as described in EP-A-0458397, or the sulphonimines of US-A-5,041,232 and US-A-5,047,163, is to be incorporated, this may be presented in the form of a second encapsulate separately from the bleach capsule or granule. Cobalt catalysts can also be used.

For peroxygen bleaching agents a suitable range are also from 0.5% to 3% avO (available Oxygen). Preferably, the

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amount of bleach material in the wash liquor is at least $12.5 \times 10^{-4}\%$ and at most 0.03% avO by weight of the liquor.

Anti-tarnishing Agents

Anti-tarnishing agents such as benzotriazole and those described in EP 723 577 (Unilever) may also be included.

Optional Ingredients

Optional ingredients are, for example, buffering agents, reducing agents, e.g., borates, alkali metal hydroxide and the well-known enzyme stabilisers such as the polyalcohols, e.g. glycerol and borax; crystal-growth inhibitors, threshold agents; perfumes and dyestuffs and the like.

Reducing agents may e.g. be used to prevent the appearance of an enzyme-deactivating concentration of oxidant bleach compound. Suitable agents include reducing sulphur-oxy acids and salts thereof. Most preferred for reasons of availability, low cost, and high performance are the alkali metal and ammonium salts of sulphuroxy acids including ammonium sulphite $(\text{NH}_4)_2\text{SO}_3$, sodium sulphite (Na_2SO_3) , sodium bisulphite (NaHSO_3) , sodium metabisulphite $(\text{Na}_2\text{S}_2\text{O}_3)$, potassium metabisulphite $(\text{K}_2\text{S}_2\text{O}_5)$, lithium hydrosulphite $(\text{Li}_2\text{S}_2\text{O}_4)$, etc., sodium sulphite being particularly preferred. Another useful reducing agent, though not particularly preferred for reasons of cost, is ascorbic acid. The amount of reducing agents to be used may vary from case to case depending on the type of bleach and the form it is in, but normally a range of about 0.01% to about 1.0% by weight, preferably from about 0.02% to about 0.5% by weight, will be sufficient.

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pH of wash liquor

The invention relates to washing processes in mechanical dish washing machines wherein the wash liquor has a low pH.

- 5 By "low pH" is meant here that the pH of the wash liquor is preferably higher than about 6.5, more preferably 7.5 or higher, most preferably 8.5 or higher. Preferably the pH is lower than about 11, more preferably lower than about 10.5, more preferably lower than about 9.5. The most advantageous
10 pH range is from 8.5 to 10.5.

When marketing the superior dishwashing composition of this invention, it is preferred that the dishwashing composition is formed into a tablet and sold in a package with

- 15 directions to add the dishwashing composition to the dishwashing machine as a 3-in-1 product. Thus, a dishwasher is charged with the dishwashing composition of this invention without having to add to the dishwasher conventional rinse aid compositions and sodium chloride. In
20 some embodiments however, compositions may also be in powder form.

Examples

- 25 The invention will now be illustrated by the following non-limiting Examples.

All percentages are on a weight basis.

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Table 1

	Example 1	Example 2	Example 3
Na Tripolyphosphate	60.60	60.0	58.7
Acusol 460ND ¹	1.6	0.3	0.6
Na EHDP Granular — Monsanto SPE 9528	1.10	1.10	1.10
PA25 CL ²	3.30	3.30	3.30
Na Disilicate —	9.7	9.7	9.7
Na Perborate Monohydrate	15.00	14.0	14.0
TAED (83%)	2.50	2.50	2.50
Protease/amylase	4.0	4.0	4.0
Nonionic ³	1.1	4.0	5.0
Minors	to 100.00	To 100	to 100

- 5 1) copolymer of diisobutylene and maleic acid, MW 15,000,
ex copolymer of diisobutylene and maleic acid, MW 15,000,
supplied by Rohm and Haas Company
- 2) acrylic acid polymer ex BASF
- 3) nonionic surfactant, ex BASF (LF 403)

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CLAIMS

1. A machine dish wash composition comprising
 - 5 a) a hydrophobically modified polycarboxylic acid
 - b) an organic phosphonates and
 - c) a polymer of acrylic acid.
- 10 2. A composition according to claim 1 in which the hydrophobically modified polycarboxylic acid is a co-polymer containing as polymerised units from 20 to 75 wt% maleic acid, maleic anhydride or salts thereof and from 25 to 80 wt% of a hydrophobe is at least one
15 monomer selected from the group consisting of isobutylene, diisobutylene, styrene, decane and eicosene;
- 20 3. A composition according to claim 1 or claim 2, wherein the hydrophobically modified polycarboxylic acid is present at a level of 0.3% to 0.6% by weight of the composition.
- 25 4. A composition according to any one of the preceding claims in which the organic phosphonate is selected from hydroxy-ethylene 1,1 diphosphonate or 2 phosphono-butane, 1,2,4 tricarboxylic acid.
- 30 5. A composition according to any one of the preceding claims in which the polymer of acrylic acid has a molecular weight between 500 and 20,000.
6. A composition according to any one of the preceding claims in which the level of antiscaling agent comprising a hydrophobically modified polycarboxylic

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acid and an organic phosphonate is from 0.5 to 5 wt% of the composition.

- 5 7. A composition further according to any one preceding claim further comprising at least 4.0 wt% of an ethoxylated and/or propoxylated nonionic surfactant in which the nonionic surfactant has a cloud point in water of 14°C or less.
- 10 8. A composition according to claim 7 in which the nonionic surfactant has a cloud point in water of 12°C or less.
- 15 9. A composition according to claim 7 or claim 8 in which the level of nonionic surfactant is from 5 to 8 wt% of the total composition.
- 20 10. A composition according to any one preceding claim comprising greater than 50 wt% of a builder
11. A composition according to claim 10 in which the builder is a water-soluble phosphate.
- 25 12. A composition according to any one preceding claim in which the composition is in the form of a tablet.
13. A composition according to any one preceding claim which is provided with instructions that no salt is to be added to the dishwashing machine.
- 30 14. A composition according to any one preceding claim which is provided with instructions that no rinse aid is to be added to the dishwashing machine.

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15. A process for washing articles in a dish washer
comprising the steps of:

5 ii) adding a composition according to any preceding claim
to the wash liquor of the dish washer followed by;

ii) treating articles requiring cleaning with the wash
liquor in a conventional manner;

10 wherein no additional rinse aid is present within the
dishwasher.

16. A process according to claim 9 wherein no salt is
15 added to the dishwasher to rejuvenate the ion
exchange.

17. A kit of parts comprising

20 (i) a composition as claimed in any one of claims 1
to 11 and;

(ii) instructions stating that no rinse aid or salt
is to be added to the dishwashing machine.

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INTERNATIONAL SEARCH REPORT

Int Application No

PCT/EP 01/12083

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C11D3/37 C11D3/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D A47L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 96 00277 A (UNILEVER) 4 January 1996 (1996-01-04) page 1, line 4 - line 15 page 2, line 1 - line 7 page 5, line 30 - page 6, line 9	1-6, 10, 17
A	page 11, line 33 - page 12, line 8; examples I, IV ---	7-9, 11, 12, 15
Y	EP 0 551 670 A (UNILEVER) 21 July 1993 (1993-07-21) abstract	1-6, 10, 17
A	page 2, line 32 - line 36 page 3, line 23 - line 57; example II --- -/--	7-9, 11, 12, 15

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

8 March 2002

Date of mailing of the international search report

21/03/2002

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 01/12083

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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International Application No

PCT/EP 01/12083

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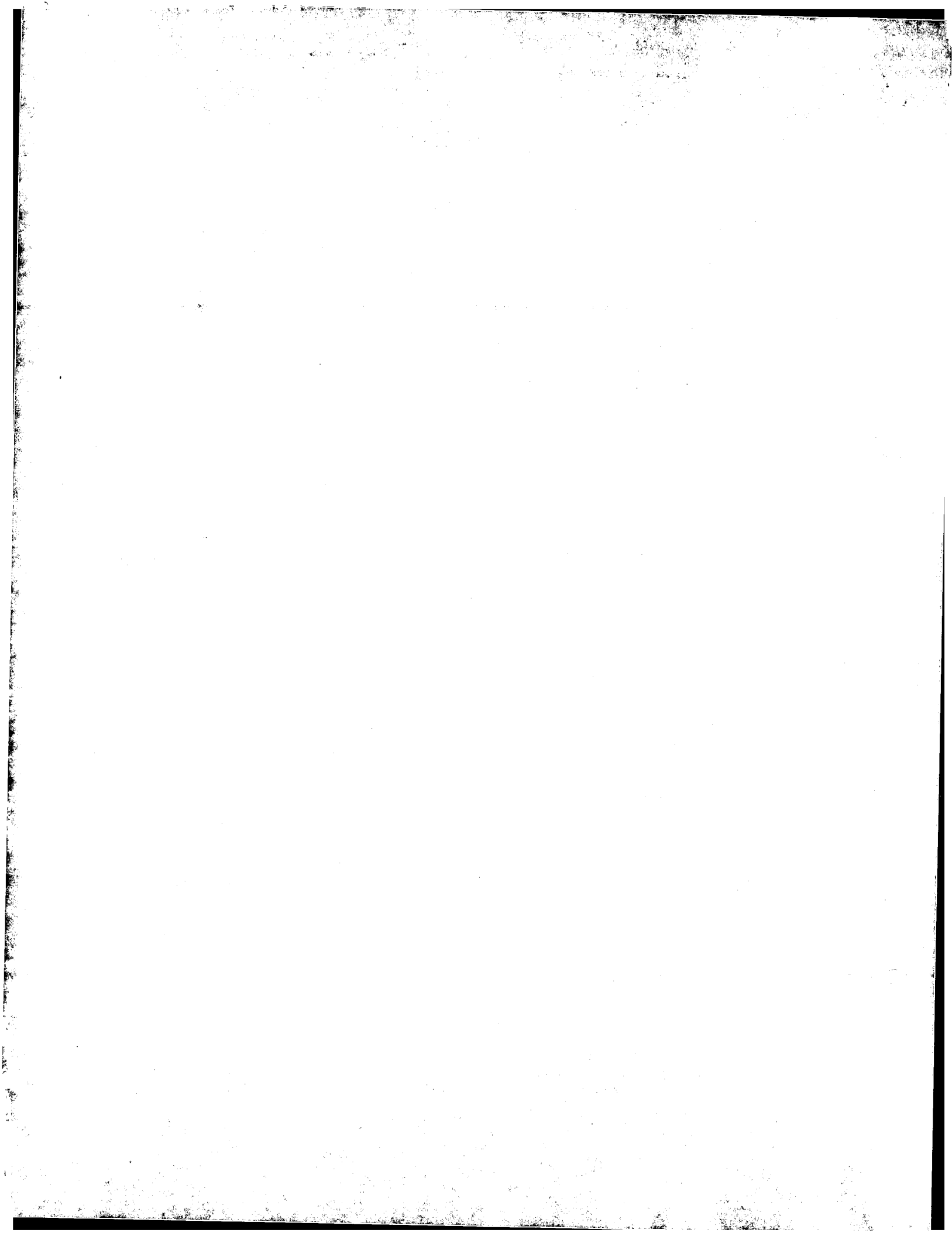
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Information on patent family members

In International Application No

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(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
2 May 2002 (02.05.2002)

PCT

(10) International Publication Number
WO 02/34870 A1

(51) International Patent Classification⁷: C11D 3/37, 3/36

(21) International Application Number: PCT/EP01/12083

(22) International Filing Date: 17 October 2001 (17.10.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
00309395.2 25 October 2000 (25.10.2000) EP

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(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: DISH-WASHING COMPOSITIONS

(57) Abstract: A machine dish wash composition comprising: a) a hydrophobically modified polycarboxylic acid b) an organic phosphonates and c) a polymer of acrylic acid.

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DISH-WASHING COMPOSITIONS

The present invention is in the field of machine dishwashing. More specifically, the invention encompasses compositions for use in a machine dish wash formulation, which do not necessitate the addition of salt or rinse aid to the machine.

To wash articles in a commercially available dish washing machine entails using three product types. Salt is added to the salt compartment to soften the water, a dishwashing formulation is used to clean the articles and a rinse aid is used to ensure that the articles are rinsed with no streaks or smears.

Consumers find it inconvenient replace the salt and rinse aid in a dish wash machine.

WO 00/06684 (Benckiser) discloses a machine dish wash tablet. The tablet has a base composition that carries out its function in the main wash cycle, and a separate core that acts as a rinse aid in the rinse cycle of the machine. However such a tablet is complicated to manufacture.

The present invention relates to a composition for washing dishes that obviates the need for salt and rinse aid in the machine dishwashing process.

Accordingly, the present invention relates to a machine dish wash composition comprising:

- a) a hydrophobically modified polycarboxylic acid
- b) an organic phosphonates and
- c) a polymer of acrylic acid.

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Also described is a process for washing articles in a dishwasher comprising the steps of:

- i) adding a composition as described in the preceding paragraph to the wash liquor of the dishwasher followed by;
- ii) treating articles requiring cleaning with the wash liquor in a conventional manner;

wherein no additional rinse aid is present within the dishwasher and no salt is present in the dishwasher to rejuvenate the ion exchange.

Also part of this inventive concept is a kit of parts comprising a composition as described above and instructions stating that no rinse aid or salt is to be added to the dishwashing machine.

Compositions according to the invention have been found to be particularly effective at antiscaling and antispotting in the machine dishwash process. In particular, with the inclusion of relatively high levels of hydrophobically modified polycarboxylic acid, this can lead to a cloudy surface appearing on e.g. glass. However the combination of ingredients which is the invention addressed these problems. A combination of antiscaling/antispotting agents are present in the composition of the invention.

The first is a hydrophobically modified polycarboxylic acid, preferably a co-polymer containing as polymerised units from 20 to 75 wt% maleic acid, maleic anhydride or salts thereof and from 25 to 80 wt% of a hydrophobe which is at least one monomer selected from the group consisting of isobutylene, diisobutylene, styrene, decane and eicosene.

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The hydrophobically modified polycarboxylic acid preferably has a molecular weight from 200 to 1 million, more preferably from 1,000 to 750,000.

- 5 A preferred hydrophobically modified polycarboxylic acid is Acusol 820, a copolymer of acrylic acid with C₁₈ and with EO₂₀C₁₈ side chains, MW about 500,000, supplied by Rohm and Haas Company; particularly preferred is Acusol 460, a co-polymer of diisobutylene and maleic acid, MW 15,000,
10 supplied by Rohm and Haas Company;

- It is preferable if the level of hydrophobically modified polycarboxylic acid is from 0.1 to 10 wt% of the total composition, more preferably from 0.5 to 7 wt%, most
15 preferably from 1 to 5 wt%. However in certain preferred embodiments, the preferred range of modified polycarboxylic acid may be from 0.1% to 10%, preferably 0.15 to 1.0%, even more preferably 0.3 to 0.6% by weight of the composition.

- 20 Organic phosphonates are also present as antiscaling agents.

- Particularly preferred antiscaling agents are organic phosphonates such as α -hydroxy-2 phenyl ethyl diphosphonate, ethylene diphosphonate, hydroxy 1,1-hexylidene, vinylidene
25 1,1 diphosphonate, 1,2 dihydroxyethane 1,1 diphosphonate and hydroxy-ethylene 1,1 diphosphonate. Most preferred is hydroxy-ethylene 1,1 diphosphonate (EDHP) and 2 phosphonobutane, 1,2,4 tricarboxylic acid (Bayhibit).

- 30 Also present are polymers and co-polymers of acrylic acid having a molecular weight between 500 and 20,000 can also be used, such as homo-polymeric polycarboxylic acid compounds with acrylic acid as the monomeric unit. The average weight of such homo-polymers in the acid form preferably ranges
35 from 1,000 to 100,000 particularly from 3,000 to 10,000.

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Also suitable are polymeric polycarboxylates are co-polymers derived from monomers of acrylic acid and maleic acid. The average molecular weight of these polymers in the acid form preferably ranges from 4,000 to 70,000.

It is preferable if the level antiscaling agent is from 0.2 to 10 wt% of the total composition, preferably from 0.5 to 5 wt%.

Preferred ratios of antiscaling agent to nonionic surfactant are 1:3 to 3:1, more preferably 1:1 to 1:2

Surfactant System

The composition also comprises a surfactant system, which preferably comprises ethoxylated and/or propoxylated nonionic surfactants, more preferably selected from nonionic ethoxylated/propoxylated fatty alcohol surfactants which preferably have a cloud point in water of 14 or less, preferably of 12 or less, most preferably 10°C or less.

Examples of suitable nonionic surfactants having the required cloud points for use in the invention are found in the low- to non-foaming ethoxylated straight-chain alcohols of the Plurafac® LF series, supplied by the BASF Company; Synperonic RA series supplied by ICI Triton® DF series, supplied by the Rohm & Haas Company.

Other suitable surfactants include epoxy capped poly (oxyalkylated) alcohols, such as e.g. SLB 18B 45, ex. Olin Chemicals.

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The surfactants are preferably present at levels of at least 4.0 wt%, preferably 4-6 wt%, more preferably 5 to 8 wt% of the total composition.

- 5 An antifoam to surpress foaming is preferably present.

If an anionic surfactant is used it is advantageously present at levels of 2 wt% or below.

10 Builder Material

The compositions of the invention may contain a builder. The builder may be a phosphate or non-phosphate builder.

- 15 Compositions of the invention preferably comprise a water-soluble phosphate builder.

Phosphate builders are particularly preferred. Specific examples of water-soluble phosphate builders are the alkali
20 metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerisation ranges from about 6 to 21, and salts of phytic acid. Sodium or potassium tripolyphosphate is most preferred.

25

The level of builder is from 35% to 90%, preferably 50% to 90% by weight, preferably from 55% to 80% by weight.

The compositions of the present invention may comprise a
30 water-soluble non-phosphate builder. Suitable examples of non-phosphorus-containing inorganic builders include water-soluble alkali metal carbonates, bicarbonates, sesquicarbonates, borates, silicates, including layered silicates such as SKS-6 ex. Clarent and metasilicates.

- 35 Specific examples include sodium carbonate (with or without

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calcite seeds), potassium carbonate, sodium and potassium bicarbonates and silicates including layered silicates.

Organic detergent builders can also be used as nonphosphate
5 builders in the present invention. Examples of organic
builders include alkali metal citrates, succinates,
malonates, fatty acid sulfonates, fatty acid carboxylates,
nitrilotriacetates, oxydisuccinates, alkyl and alkenyl
disuccinates, oxydiacetates, carboxymethyloxy succinates,
10 ethylenediamine tetraacetates, tartrate monosuccinates,
tartrate disuccinates, tartrate monoacetates, tartrate
diacetates, oxidised starches, oxidised heteropolymeric
polysaccharides, polyhydroxysulfonates, polycarboxylates
such as polyacrylates, polymaleates, polyacetates,
15 polyhydroxyacrylates, polyacrylate/polymaleate and
polyacrylate/ polymethacrylate copolymers,
acrylate/maleate/vinyl alcohol terpolymers,
aminopolycarboxylates and polyacetal carboxylates, and
polyaspartates and mixtures thereof. Such carboxylates are
20 described in U.S. Patent Nos. 4,144,226, 4,146,495 and
4,686,062. Alkali metal citrates, nitrilotriacetates,
oxydisuccinates, acrylate/maleate copolymers and
acrylate/maleate/vinyl alcohol terpolymers are especially
preferred nonphosphate builders.

25

Silica

Silica material may be included in the composition.
Suitable forms of silica include amorphous silica, such as
30 precipitated silica, pyrogenic silica and silica gels, such
as hydrogels, xerogels and aerogels, or the pure crystal
forms quartz, tridymite or cristobalite, but the amorphous
forms of silica are preferred. Suitable silicas may readily
be obtained commercially. They are sold, for example under
35 the Registered Trade Name Gasil 200 (ex Crosfield, UK).

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Preferably, the silica is in the product in such a form that it can dissolve when added to the wash liquor. Therefore, addition of silica by way of addition anti-foam particles of silica and silicone oil is not preferred.

Therefore, it is preferred that silica material are used that have a particle size (as determined with a Malvern Laser, i.e. "aggregated" particles size) of at most $40\mu\text{m}$, most preferably at most $20\mu\text{m}$ provides better results in the wash. In view of incorporation in a cleaning composition, it is preferred that the particle size of the silica material is at least $1\mu\text{m}$, more preferably at least $2\mu\text{m}$, and most preferably at least $5\mu\text{m}$.

Preferably, the silica material is present in the cleaning composition at a level of at least 0.1%, more preferably at least 0.5%, most preferably at least 1% by weight of the cleaning composition and preferably at most 10%, more preferably at most 8%, most preferably at most 5% by weight of the cleaning composition.

Silicates

The composition optionally comprises alkali metal silicates. When silicates are present, the SiO_2 level should be from 1% to 35%, preferably from 2% to 20%, more preferably from 3% to 10%, based on the weight of the automatic dishwasher detergent. The ratio of SiO_2 to the alkali metal oxide (M_2O , where M = alkali metal) is typically from 1 to 3.5, preferably from 1.6 to 3, more preferably from 2 to 2.8. Preferably, the alkali metal silicate is hydrous, having from 15% to 25% water, more preferably from 17% to 20%.

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The highly alkali metasilicates can in general be employed, although the less alkaline hydrous alkali metal silicates having a $\text{SiO}_2:\text{M}_2\text{O}$ ratio of from 2.0 to 2.4 are, as noted, greatly preferred. Anhydrous forms of the alkali metal
5 silicates with a $\text{SiO}_2:\text{M}_2\text{O}$ ratio of 2.0 or more are also less preferred because they tend to be significantly less soluble than the hydrous alkali metal silicates having the same ratio.

10 Sodium and potassium, and especially sodium, silicates are preferred. A particularly preferred alkali metal silicate is a granular hydrous sodium silicate having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of from 2.0 to 2.4 available from PQ Corporation, named Britesil H20 and Britesil H24. Most preferred is a
15 granular hydrous sodium silicate having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of 2.0. While typical forms, i.e. powder and granular, of hydrous silicate particles are suitable, preferred silicate particles having a mean particle size between 300 and 900 microns and less than 40% smaller than 150 microns and less
20 than 5% larger than 1700 microns. Particularly preferred is a silicate particle with a mean particle size between 400 and 700 microns with less than 20% smaller than 150 microns and less than 1% larger than 1700 microns. Compositions of the present invention having a pH of 9 or less preferably
25 will be substantially free of alkali metal silicate.

Enzymes

Enzymes may be present in the compositions of the invention.

30 Examples of enzymes suitable for use in the cleaning compositions of this invention include lipases, peptidases, amylases (amylolytic enzymes) and others which degrade, alter or facilitate the degradation or alteration of biochemical soils and stains encountered in cleansing
35 situations so as to remove more easily the soil or stain

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from the object being washed to make the soil or stain more removable in a subsequent cleansing step. Both degradation and alteration can improve soil removal.

- 5 Well-known and preferred examples of these enzymes are lipases, amylases and proteases. The enzymes most commonly used in machine dishwashing compositions are amylolytic enzymes. Preferably, the composition of the invention also contains a proteolytic enzyme. Enzymes may be present in a
10 weight percentage amount of from 0.2 to 7% by weight. For amylolytic enzymes, the final composition will have amylolytic activity of from 10^2 to 10^6 Maltose units/kg. For proteolytic enzymes the final composition will have proteolytic enzyme activity of from 10^6 to 10^9 Glycine
15 Units/kg.

Bleach Material

- Bleach material is preferably incorporated in the
20 composition.

The bleach material may be a chlorine- or bromine-releasing agent or a peroxygen compound. Peroxygen based bleach materials are however preferred.

25

- Organic peroxy acids or the precursors therefor are typically utilized as the bleach material. The peroxyacids usable in the present invention are solid and, preferably, substantially water-insoluble compounds. By "substantially
30 water-insoluble" is meant herein a water-solubility of less than about 1% by weight at ambient temperature. In general, peroxyacids containing at least about 7 carbon atoms are sufficiently insoluble in water for use herein.

- 10 -

Inorganic peroxygen-generating compounds are also typically used as the bleaching material of the present invention. Examples of these materials are salts of monopersulphate, perborate monohydrate, perborate tetrahydrate, and
5 percarbonate.

Monoperoxy acids useful herein include alkyl peroxy acids and aryl peroxyacids such as peroxybenzoic acid and ring-substituted peroxybenzoic acids (e.g. peroxy-alpha-naphthoic acid); aliphatic and substituted aliphatic
10 monoperoxy acids (e.g. peroxy lauric acid and peroxy stearic acid); and phthaloyl amido peroxy caproic acid (PAP).

Typical diperoxy acids useful herein include alkyl diperoxy acids and aryldiperoxy acids, such as 1,12-di-peroxy-dodecanedioic acid (DPDA); 1,9-diperoxyazelaic acid, diperoxybrassylic acid, diperoxysebacic acid and diperoxy-isophthalic acid; and 2-decyldiperoxybutane-1,4-dioic acid.

Peroxyacid bleach precursors are well known in the art. As non-limiting examples can be named N,N,N',N'-tetraacetyl ethylene diamine (TAED), sodium nonanoyloxybenzene sulphonate (SNOBS), sodium benzoyloxybenzene sulphonate (SBOBS) and the cationic peroxyacid precursor (SPCC) as
20 described in US-A-4,751,015.

If desirably a bleach catalyst, such as the manganese complex, e.g. Mn-Me TACN, as described in EP-A-0458397, or the sulphonimines of US-A-5,041,232 and US-A-5,047,163, is
30 to be incorporated, this may be presented in the form of a second encapsulate separately from the bleach capsule or granule. Cobalt catalysts can also be used.

For peroxygen bleaching agents a suitable range are also
35 from 0.5% to 3% avO (available Oxygen). Preferably, the

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amount of bleach material in the wash liquor is at least $12.5 \times 10^{-4}\%$ and at most 0.03% avO by weight of the liquor.

Anti-tarnishing Agents

5

Anti-tarnishing agents such as benzotriazole and those described in EP 723 577 (Unilever) may also be included.

Optional Ingredients

10

Optional ingredients are, for example, buffering agents, reducing agents, e.g., borates, alkali metal hydroxide and the well-known enzyme stabilisers such as the polyalcohols, e.g. glycerol and borax; crystal-growth inhibitors,
15 threshold agents; perfumes and dyestuffs and the like.

Reducing agents may e.g. be used to prevent the appearance of an enzyme-deactivating concentration of oxidant bleach compound. Suitable agents include reducing sulphur-oxy acids
20 and salts thereof. Most preferred for reasons of availability, low cost, and high performance are the alkali metal and ammonium salts of sulphuroxy acids including ammonium sulphite $((\text{NH}_4)_2\text{SO}_3)$, sodium sulphite (Na_2SO_3) , sodium bisulphite (NaHSO_3) , sodium metabisulphite $(\text{Na}_2\text{S}_2\text{O}_3)$,
25 potassium metabisulphite $(\text{K}_2\text{S}_2\text{O}_5)$, lithium hydrosulphite $(\text{Li}_2\text{S}_2\text{O}_4)$, etc., sodium sulphite being particularly preferred. Another useful reducing agent, though not particularly preferred for reasons of cost, is ascorbic acid. The amount of reducing agents to be used may vary from
30 case to case depending on the type of bleach and the form it is in, but normally a range of about 0.01% to about 1.0% by weight, preferably from about 0.02% to about 0.5% by weight, will be sufficient.

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pH of wash liquor

The invention relates to washing processes in mechanical dish washing machines wherein the wash liquor has a low pH.

- 5 By "low pH" is meant here that the pH of the wash liquor is preferably higher than about 6.5, more preferably 7.5 or higher, most preferably 8.5 or higher. Preferably the pH is lower than about 11, more preferably lower than about 10.5, more preferably lower than about 9.5. The most advantageous
10 pH range is from 8.5 to 10.5.

When marketing the superior dishwashing composition of this invention, it is preferred that the dishwashing composition is formed into a tablet and sold in a package with
15 directions to add the dishwashing composition to the dishwashing machine as a 3-in-1 product. Thus, a dishwasher is charged with the dishwashing composition of this invention without having to add to the dishwasher conventional rinse aid compositions and sodium chloride. In
20 some embodiments however, compositions may also be in powder form.

Examples

- 25 The invention will now be illustrated by the following non-limiting Examples.

All percentages are on a weight basis.

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Table 1

	Example 1	Example 2	Example 3
Na Tripolyphosphate	60.60	60.0	58.7
Acusol 460ND ¹	1.6	0.3	0.6
Na EHDP Granular — Monsanto SPE 9528	1.10	1.10	1.10
PA25 CL ²	3.30	3.30	3.30
Na Disilicate —	9.7	9.7	9.7
Na Perborate Monohydrate	15.00	14.0	14.0
TAED (83%)	2.50	2.50	2.50
Protease/amylase	4.0	4.0	4.0
Nonionic ³	1.1	4.0	5.0
Minors	to 100.00	To 100	to 100

- 5 1) copolymer of diisobutylene and maleic acid, MW 15,000,
ex copolymer of diisobutylene and maleic acid, MW 15,000,
supplied by Rohm and Haas Company
- 2) acrylic acid polymer ex BASF
- 3) nonionic surfactant, ex BASF (LF 403)

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CLAIMS

1. A machine dish wash composition comprising
 - 5 a) a hydrophobically modified polycarboxylic acid
 - b) an organic phosphonates and
 - c) a polymer of acrylic acid.
- 10 2. A composition according to claim 1 in which the hydrophobically modified polycarboxylic acid is a co-polymer containing as polymerised units from 20 to 75 wt% maleic acid, maleic anhydride or salts thereof and from 25 to 80 wt% of a hydrophobe is at least one monomer selected from the group consisting of
 - 15 isobutylene, diisobutylene, styrene, decane and eicosene;
- 20 3. A composition according to claim 1 or claim 2, wherein the hydrophobically modified polycarboxylic acid is present at a level of 0.3% to 0.6% by weight of the composition.
- 25 4. A composition according to any one of the preceding claims in which the organic phosphonate is selected from hydroxy-ethylene 1,1 diphosphonate or 2 phosphonobutane, 1,2,4 tricarboxylic acid.
- 30 5. A composition according to any one of the preceding claims in which the polymer of acrylic acid has a molecular weight between 500 and 20,000.
6. A composition according to any one of the preceding claims in which the level of antiscaling agent comprising a hydrophobically modified polycarboxylic

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acid and an organic phosphonate is from 0.5 to 5 wt% of the composition.

- 5 7. A composition further according to any one preceding claim further comprising at least 4.0 wt% of an ethoxylated and/or propoxylated nonionic surfactant in which the nonionic surfactant has a cloud point in water of 14°C or less.
- 10 8. A composition according to claim 7 in which the nonionic surfactant has a cloud point in water of 12°C or less.
- 15 9. A composition according to claim 7 or claim 8 in which the level of nonionic surfactant is from 5 to 8 wt% of the total composition.
- 20 10. A composition according to any one preceding claim comprising greater than 50 wt% of a builder
11. A composition according to claim 10 in which the builder is a water-soluble phosphate.
- 25 12. A composition according to any one preceding claim in which the composition is in the form of a tablet.
13. A composition according to any one preceding claim which is provided with instructions that no salt is to be added to the dishwashing machine.
- 30 14. A composition according to any one preceding claim which is provided with instructions that no rinse aid is to be added to the dishwashing machine.

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15. A process for washing articles in a dish washer
comprising the steps of:

5 ii) adding a composition according to any preceding claim
to the wash liquor of the dish washer followed by;

ii) treating articles requiring cleaning with the wash
liquor in a conventional manner;

10 wherein no additional rinse aid is present within the
dishwasher.

16. A process according to claim 9 wherein no salt is
15 added to the dishwasher to rejuvenate the ion
exchange.

17. A kit of parts comprising

20 (i) a composition as claimed in any one of claims 1
to 11 and;

(ii) instructions stating that no rinse aid or salt
is to be added to the dishwashing machine.

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INTERNATIONAL SEARCH REPORT

Int Application No
PCT/EP 01/12083

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/37 C11D3/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D A47L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

8 March 2002

Date of mailing of the international search report

21/03/2002

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INTERNATIONAL SEARCH REPORT

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